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PART D

ANALYTICAL METHODS

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INTRODUCTION:

Liquid crystalline compounds as stationary phases have been used in gas chromatography for isomer specific separations (1). The separation mechanism is based on molecular size and shape of the solutes. On liquid crystalline phases linear and planar solute molecules are retained longer than bulkier and non linear solutes of similar chemical and physical properties. The application of high temperature nematic liquid crystals for the separation of three to seven ring polycyclic aromatic hydrocarbon and PCB isomers of environmental importance have been demonstrated (2-6). The isomer-specific separation of positional, geometrical and optical isomers are reported using low molecular weight monomeric liquid crystalline stationary phases (7-10). There are several difficulties in using monomeric liquid crystals in capillary columns to achieve higher efficiency and selectivity (11-13).

Recently, polymeric liquid crystals (PLC) have been developed for use in capillary gas chromatography. Finkelmann first reported the use of liquid crystalline polysiloxane (LCPS) stationary phases in gas chromatography (14). Since then a number of reports have appeared on the applications and development of PLC stationary phases for isomer specific separations (15-21). Lee has developed several LCPS stationary phases and demonstrated the usefulness of these phases in the analysis of important complex environmental mixtures (22). It has been shown that PLC capillary columns have a high isomer specific selectivity and efficiencies comparable to those of conventional columns.

These highly selective columns should be useful for the separation and quantitation of complex samples containing PCDD, PCDF and PCB. There are 75 PCDD and 135 PCDF isomers. Separation of those isomers from other compounds present in complex environmental samples is very difficult. In particular, separation of these compounds from high concentrations of PCB is challenging. Selectivity based on molecular weight can be achieved using the GC-MS/EISIM mode for the detection of PCDD and PCDF from co-eluting compounds of different molecular weight. However, the fragment ions of certain co-eluting compounds such as PCB interfere in the analysis of PCDD and PCDF. If interfering compounds can be separated prior to their analysis by GC-MS/EISIM technique positive identification and quantitation of PCDD and PCDF is possible using various criteria (23).

This paper shows the unique selectivity of LCPS capillary column for the separation of 2,3,7,8-TCDD and TCDF from other tetra isomers. The separation of large number of tetra- to octa-chloro dioxins and dibenzofuran isomers is compared with the DB-5

column. The quantitative analysis of 2,3,7,8-TCDD and TCDF and all PCDD and PCDF in an extract of flyash from a municipal incinerator in a single GC-MS run and separation of 2,3,7,8-TCDD and TCDF from sample with high PCB content accomplished on an LCPS column.

EXPERIMENTAL SECTION:

The Gas Chromatograph used was a Hewlett Packard model 5880, equipped with electron capture dector(ECD) and a cool-on column injector. The GC-MS system used was a Hewlett Packard 5987 with an HP1000 data system, cool-on column injector, and splitless direct interface between the GC and MS.

Flyash samples were soxhlet extracted for 48 hours using benzene. Benzene extracts were concentrated to 5 to 25 ul/gram flyash. In the GC-MS/EISIM analysis, the ion source temperature was 200 C. The ions monitored for the tetra to octa chlorodioxins and furans were M, M+2, M+4 or M+2, M+4, M+6 for each congener group. The retention windows were determined by analysis of a Ontario flyash extract that contained all PCDD and PCDF. Selectivity of column for separation of 2,3,7,8-TCDD and TCDF was confirmed from retention time of standards. The quantitation of 2,3,7,8-tetra chlorodibenzodioxin and furan isomers was carried out using external standards. For the quantitation of total PCDD and PCDF congeners an external standard containing one isomer of each congener group from tetra- to octa-chloro dioxins and dibenzofurans was used. Concentrations of all PCDD and PCDF standards were from 100 to 500 pg/ul.

RESULTS AND DISCUSSION:

Analytical methodology can be simplified if a gas chromatographic column can separate the interfering compounds, as well as, the isomers in all congener groups. Figure 1 and 2 contrast the separation of the tetra- to octa- chlorodibenzo-dioxins in a flyash extract on a liquid crystalline polysiloxane (LCPS) column with the DB-5 column. A similar contrast for the separation of the tetra- to octa- chlorodibenzofurans in the flyash extract is shown in figure 3 and 4. Identification of PCDD and PCDF congeners was carried out by monitoring three characteristic ions such as M, M+2, M+4 for the tetra to hexa chloro substituted congeners and M+2, M+4, M+6 for the hepta and octa chloro substituted congeners. The peaks present in the three characteristic ions, for a congener group, in proper intensity ratios and retention windows were the identification criteria used for the respective congener group isomers. Mass

chromatograms of the most intense ions of each congener group are shown in figures 1 to 4. The separation on the LCPS column is clearly different than that on the DB-5 column. Retention behaviour on the non polar DB-5 column is based on the boiling points of the solute molecules. The separation of large number of PCDD and PCDF isomers in a congener group could not be observed on the DB-5 column presumably due to their similar boiling points. Separation on the LCPS stationary phase depends on the shape, polarity and the boiling points of the solute molecules. This gives a pronounced separation of several isomers in a congener group on the LCPS column. The separations of large number of isomers in congener groups observed on the LCPS column are comparable to that on long polar columns (24, 25).

The toxicity of individual isomers of PCDD and PCDF depends upon the degree of chlorination and position of chlorine substitution on the dibenzodioxin and dibenzofuran structures. Because of difficulties in separation and non availability of several isomers, the quantitative results are presented as the total amount of all the isomers present in a congeners group. However, the true assessment of toxicity of a particular sample depends upon the separation, positive identification and quantitation of the most toxic isomers. Tetrachlorodibenzodioxins (TCDD) and tetrachlorodibenzofurans (TCDF) have shown higher toxicity than the rest of the isomers, in particular 2,3,7,8-TCD and 2,3,7,8-TCDF are recognized as the most toxic isomers fr the animal tests. The study of the retention behaviour a separation of 2,3,7,8- TCDD and TCDF using very long capilla columns with different stationary phases shows that a separati of 7 to 17 out of 22 TCDD isomers and 28 out of 38 TCDF isome can be achieved on different columns (23). The LCPS capilla column used in this study shows separation of 16 TCDD and 27 TC isomers present in the flyash extract. It is clear from t figures 1 and 3 that the LCPS column can give isomer specif separation of 2,3,7,8-TCDD and TCDF, as well as, the penta- octa-chloroisomers. Selectivity shown by the LCPS column 2,3,7,8-TCDD and TCDF is unique. In all the tetra isomers, 2,3,7,8-TCDD isomer has a highly symmetrical structure and large length to breadth ratio. Thus, based on the mechanism separation on liquid crystal stationary phases, it is retai longer than other tetra isomers. Similarly, the longer retent time and separation of 2,3,7,8-TCDF from all tetrachlorofu isomers can be explained. The separations of the most to isomers were confirmed by spiking the flyash extract with carb 13 labelled 2,3,7,8-TCDD and TCDF. Their mass chromatograms shown in figure 1 and 3.

A comparative study of quantitative analysis of PCDD

PCDF in flyash samples from the Paris Tiru incinerator (France), Hiroshima incinerator (Japan) shows that the results obtained on the LCPS column and DB-5 columns are comparable. However the LCPS column, in addition gave quantitative analysis of the most toxic 2,3,7,8-TCDD and TCDF isomers in the same run. It is interesting to note that 2,3,7,8-TCDF elute after 2,3,7,8-TCDD on polar columns(24). However, on the LCPS , DB-5 and OV-101 columns retention order is reverse. The LCPS column provide a simple and fast analytical technique for separation of PCDD, PCDF and the most toxic 2,3,7,8-TCDD and TCDF isomers in complicated environmental samples.

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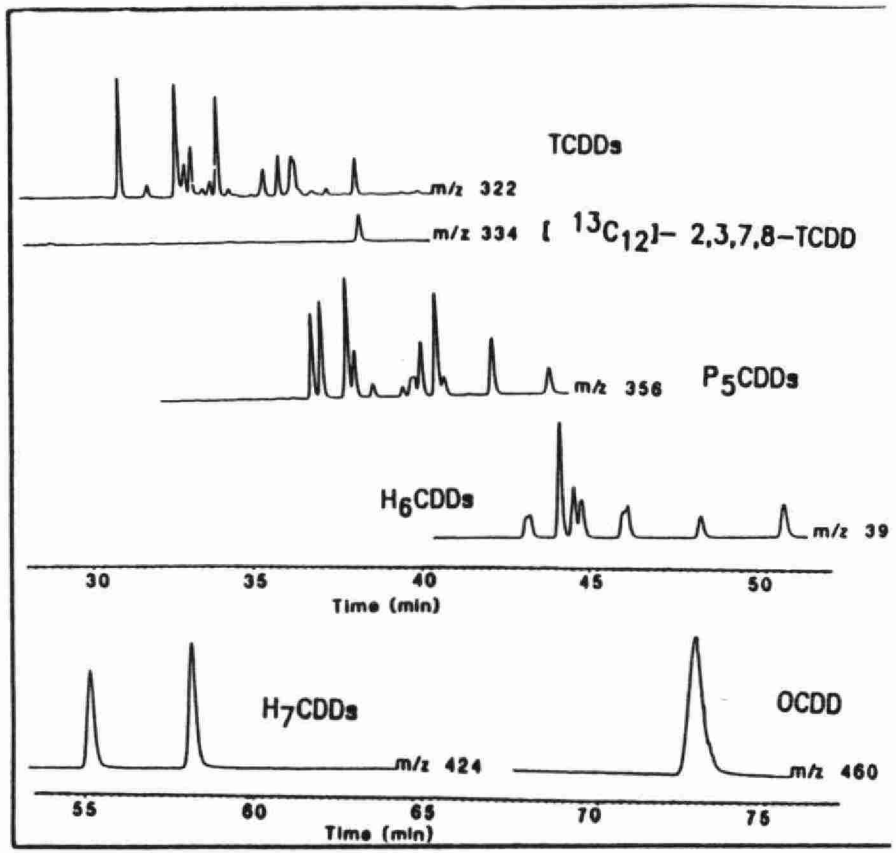

Figure 1. Separation of PCDDs in Ontario flyash extract: mass chromatograms of m/z 322 (TCDDs), m/z 334 [$^{13}C_{12}$-2,3,7,8-TCDD], m/z 356 (P_5CDDs), m/z 390 (H_6CDDs), m/z 424 (H_7CDDs), m/z 460 (OCDD). Chromatographic conditions were as follows: 20 m X 0.25 mm i. d. LCPS fused silica column; temperature at 80 ^{0}C for 1 min, programmed to 245 ^{0}C at 4 ^{0}C/min, then to 280 ^{0}C at 2 ^{0}C/min, 30 min at 280 ^{0}C.

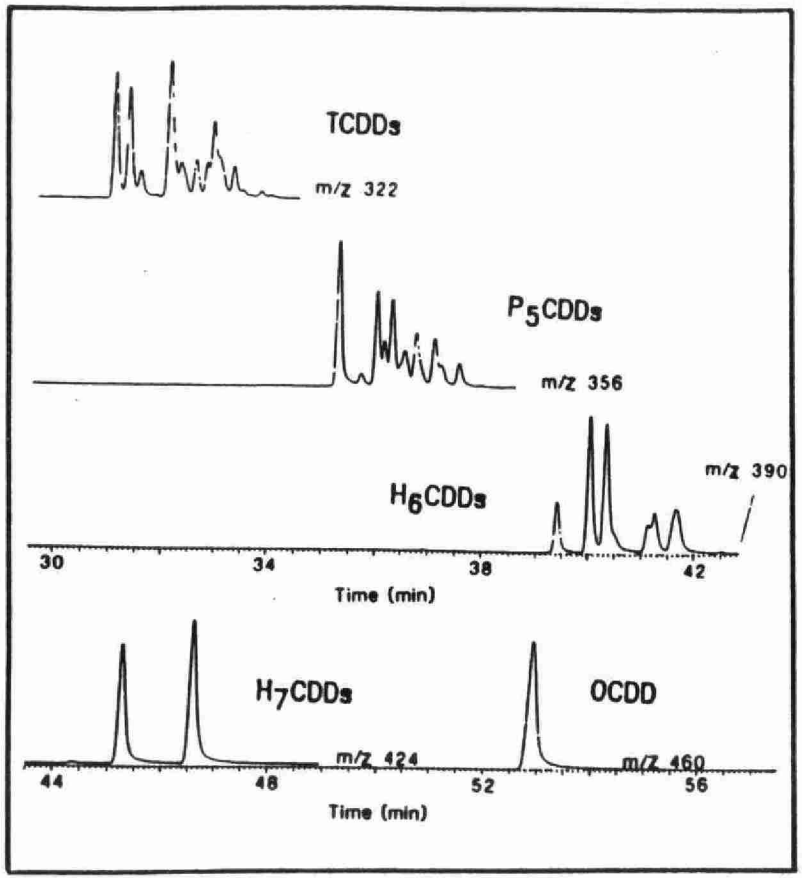

Figure 2. Separation of PCDDs in Ontario flyash extract: mass chromatograms of m/z 322 (TCDDs), m/z 356 (P_5CDDs), m/z 390 (H_6CDDs), m/z 424 (H_7CDDs), m/z 460 (OCDD).

Chromatographic conditions were as follows:

30 m X 0.32 mm i. d. DB-5 fused silica column; temperature at 80 ^{0}C for 1 min, programmed to 300 ^{0} C at 4 ^{0}C/min, 5 min at 300 ^{0}C.

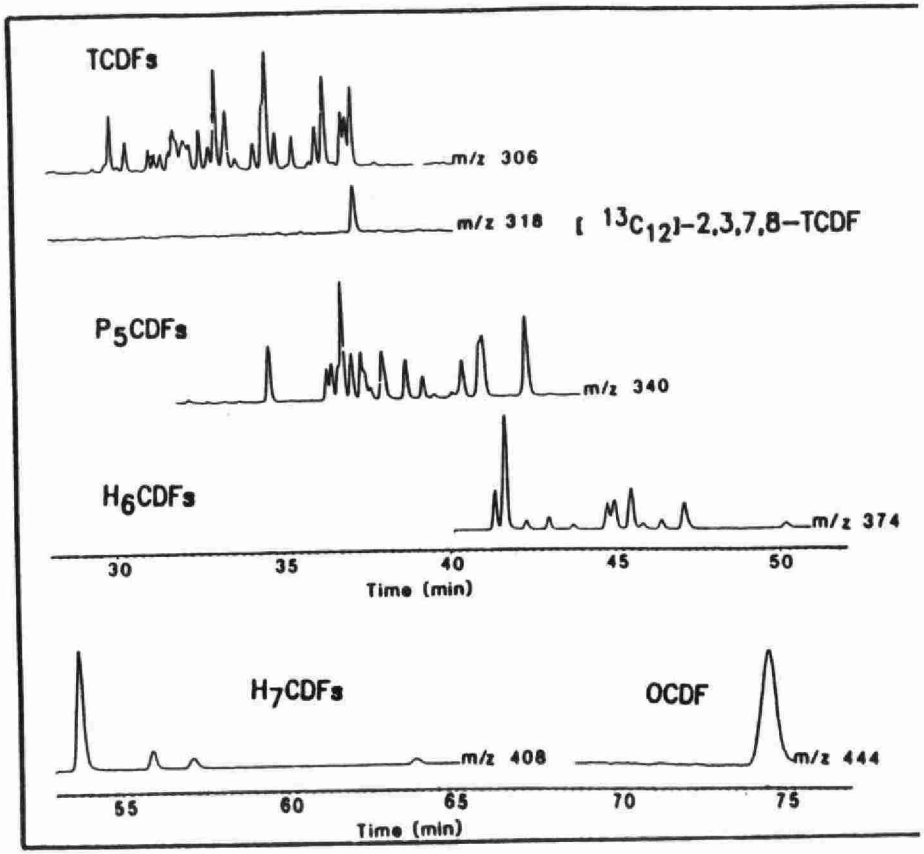

Figure 3. Separations of PCDF in Ontario flyash extract: mass chromatograms of m/z 306 (TCDFs), m/z 318 [$^{13}C_{12}$-2,3,7,8-TCDF] m/z 340 (P_5CDFs), m/z 374 (H_6CDF), m/z 408 (H_7CDF), m/z 444 (OCDF).

Chromatographic conditions were as follows:

20 m X 0.25 mm i. d. LCPS fused silica column; temperature at 80^{0}C for 1 min, programmed to 245 ^{0}C at 4 ^{0}C/min, then to 280 ^{0}C at 2 ^{0}C/min, 30 min at 280 ^{0}C.

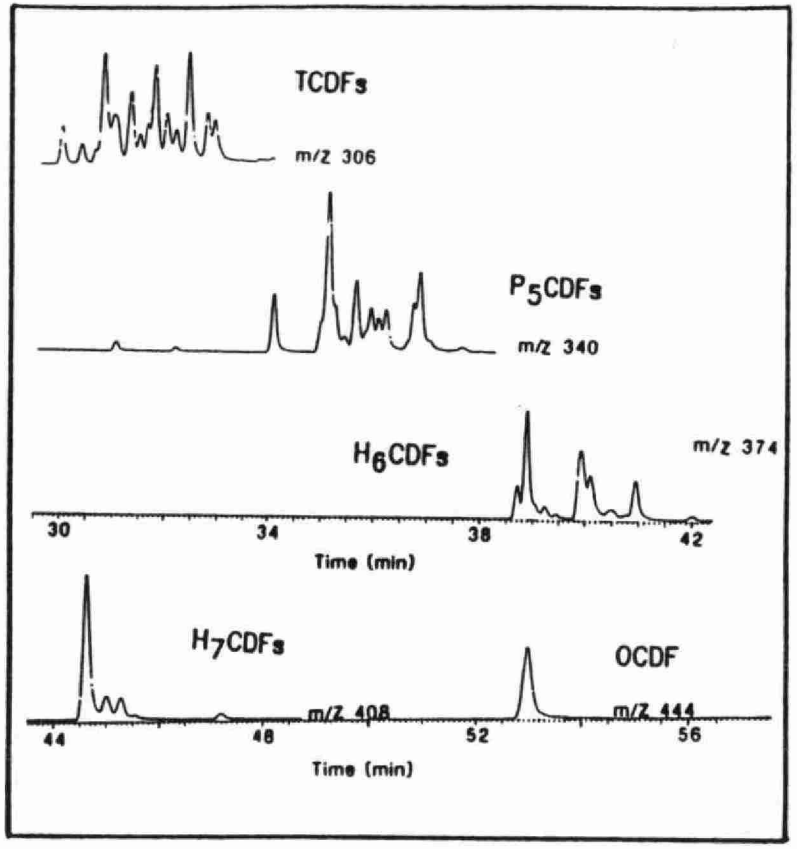

Figure 4. Separations of PCDF in Ontario flyash extract: mass chromatograms of m/z 306 (TCDFs), m/z 340 (P_5CDFs), m/z 374 (H_6CDF), m/z 408 (H_7CDF), m/z 444 (OCDF).
Chromatographic conditions were as follows:
30 m X 0.32 mm i. d. DB-5 fused silica column; temperature at 80 ^{0}C for 1 min, programmed to 300 ^{0} C at 4 ^{0}C/min, 5 min at 300 ^{0}C.